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Shear elastic modulus of magnetic gels with random distribution of magnetizable particles

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Abstract. Magnetic gels present new type of composite materials with rich set of uniquie physical properties, which find active applications in many industrial and bio-medical technologies. We present results of mathematically strict theoretical study of elastic modulus of these systems with randomly distributed magnetizable particles in an elastic medium. The results show that an external magnetic field can pronouncedly increase the shear modulus of these composites.

1. Introduction

Magnetic gels and elastomers are composites of fine magnetic particles in soft polymer matrixes. Coupling of rich set of physical properties of polymer and magnetic materials is very promising for many modern and perspective technologies. Discussions of technical and biomedical application of these systems can be found, for example, in [1-12]. A short overview of works on mechanical properties and behavior of magnetic polymers is given in [13].

Uniaxial elongation and magnetostriction effects in magnetic gels have been studied in many works (see, for example [13-19]). The shear deformations of these systems also present significant interest both from scientific and practical points of view. Theoretical studies of the shear effects in the composites with the particles, united in linear chain-like aggregates, have been done in [20-22]. The general conclusion of these works is that an external magnetic field can significantly increase the shear modulus of these composites.

As a rule, the chain-like aggregates appear in magnetic polymers on the stage preceding the composite curing due to the action of an external magnetic field (field of polymerization). On the other hand, very often magnetic gels are prepared without this field. The spatial distribution of particles in these systems is rather random and isotropic (see, for example, [15, 17, 23]). The aim of this work is theoretical study of effect of an external magnetic field on the shear elastic modulus of magnetic gels with homogeneous and isotropic distribution of non Brownian particles in a continuous matrix. It should be noted that usually the Brownian effects are negligible for the magnetic particles with the diameter 100nm and more. Composites with the particles of these sizes present the main interest from the point of view of the magnetomechanic effects, since these effects in the systems with the smaller particles, as a rule, are very weak.

The matrix is supposed elastic with the linear law of deformation and incompressible. It should be noted that the last condition is fulfilled not for all gels; however, it allows us to restrict calculations and to get the final results in transparent forms. Analysis of effects of the composite compressibility can be considered as a natural generalization of this model.

The principal and not overcome problem of the theory of composite materials is account of multiparticle interactions, both the direct ones and interactions through the perturbations of the current matrix. Usually these effects are taken into account by using various empirical and semi empirical approaches, which accuracy a priori is unknown [24].

In order to achieve mathematically rigorous results, here we will consider the systems with low concentration of the particles and neglect any interactions between them. One needs to admit that the low-concentrated systems are not very interesting from the practical point of view. However this limiting model allows us to avoid intuitive and heuristic constructions. That is why the strict results can be considered as a robust asymptotic background for the analysis of the concentrated system with the interacting particles.

The structure of the paper is the following. In the part 2 we study the composite with identical spherical magnetically hard particles; each particle has a permanent magnetic moment bounded with the particle body. The part 3 deals with the systems of magnetically soft ellipsoidal particles with random orientations of the ellipsoids axes.

2. Magnetically hard particles

We consider a system of identical spherical non Brownian particles embedded in an elastic continuous medium. All particles have the permanent magnetic moment m “frozen” in the particle body. This means that the moment can turn round only with the particle. We suppose that the volume concentration φ of the particles is low and will neglect any interactions between them.

Let us suppose that the composite is placed in a uniform magnetic field H and experiences small shear deformation in the plane perpendicular to the field. Since the concentration of the particles in the composite is supposed small, we will not take into account the difference between the external field H and the field inside the sample.

It is convenient to introduce a Cartesian coordinate system with the axis Oz in the field direction and the axis Ox in the direction of the shear. By using the mathematical similarity between the Navier– Stokes equation of Newtonian incompressible fluid flow and the Lame equation of deformation of an elastic incompressible medium [24], as well as the results of theory of dilute magnetic fluids (see, for example, [25]), one can present the needed component of the macroscopic (measurable) stress σ in the composite as:

$$\sigma = G_0(1 + 2.5\varphi)\gamma + \mu_0 \frac{m}{2v} < \mathrm{e}_x > H, \qquad \sigma = \sigma_{xz} \ . \tag{1}$$

Here G_0 is the shear modulus of the pure polymer matrix, $\gamma = \frac{\partial u_x}{\partial z}$, u_x is the component of the macroscopic (measurable) vector $\boldsymbol{u}$ of the composite displacement, μ_0 is the magnetic permeability of vacuum, v is volume of the particle, e_x is the component of the unit vector $\boldsymbol{e}$ directed along the magnetic moment $\boldsymbol{m}$ of a particle, the angle brackets <…> mean the averaging over the orientations of all particles. Our aim now is to determine the mean component $< e_x >$.

To this end we will consider an arbitrary particle situated in the field $\boldsymbol{H}$ and denote by $\boldsymbol{e}_0$ its initial (before the composite deformation) vector $\boldsymbol{e}$. Taking into account the mathematical identity of the Navier–Stokes and Lame equations and using the equations [25-27] of dynamics of a spherical non-Brownian magnetic particle in a viscous fluid, after simple transformations we come to the following equations for the components e_x and e_z of the unit vector $\boldsymbol{e}$ of orientation of an arbitrary particle:

$$\begin{gathered} \delta e_x = \frac{1}{2}\gamma e_z - \kappa e_x e_z \\ \delta e_z = -\frac{1}{2}\gamma e_x + \kappa(1 - e_z^2) \\ \kappa = \frac{\mu_0 m H}{6 G_0 v} \end{gathered} \tag{2}$$

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Here $\delta e_i = e_i - e_{i0},\ i = x, z,\ e_{i0}$ is the initial (before macroscopic shear and the field application) component of the particle vector $\boldsymbol{e}$. It should be noted that the equations (2) are derived in the linear approximation with respect to the shear strain γ.

After simple transformations in the linear approximation in γ we get:

$$\delta e_x = \frac{1}{2}\gamma\left(\frac{e_{z0}}{1+\kappa e_{z0}} + \frac{1-e_{z0}^2+e_{x0}^2}{(1+\kappa e_{z0})(1+2\kappa e_{z0})}\right) - \kappa^2\frac{e_{x0}(1-e_{z0}^2)}{(1+\kappa e_{z0})(1+2\kappa e_{z0})}\ . \tag{3}$$

We suppose that initially the particles had random orientation of their magnetic moments, i.e. $< e_{x0} > = 0$. Therefore

$$< e_x > = < e_{x0} > + < \delta e_{x0} > = < \delta e_{x0} >\ . \tag{4}$$

It is convenient to introduce the spherical coordinate system with the polar θ and azimuthal ϕ angles, so that:

$$e_{z0} = \cos\theta,\quad e_{x0} = \sin\theta\cos\phi\ . \tag{5}$$

By using (5), one can get:

$$< \delta e_x > = \frac{1}{4\pi}\int_0^{\pi}\sin\theta \mathrm{d}\theta \int_0^{2\pi}\delta e_x \mathrm{d}\phi. \tag{6}$$

Substituting (3) and (5) into (6), we obtain:

$$< \delta e_x > = \frac{1}{4}\gamma\left(\int_{-1}^{1}\frac{x}{1+\kappa x}\mathrm{d}x + 1.5\int_{-1}^{1}\frac{1-x^2}{(1+\kappa x)(1+2\kappa x)}\mathrm{d}x\right). \tag{7}$$

The integrals (7) can be calculated analytically; however, they have cumbersome forms, that is why we omit these forms here.

Parameter κ presents the ratio of the magnetic and elastic torques, acting on the particle. The Lame equations of the elastic deformation of a continuum are valid only in the case of small deformations of this medium. In part, this means that the angle of the particle turn, under the action of the magnetic and elastic torques, must be small for these equations applicability. This leads to the condition $\kappa < 1$ of restriction of the linear approximation.

Combining equations (7) and (1), we come to the following relations:

$$\sigma = G_1\gamma\ ,$$

$$G_1 = G_0\left(1 + \frac{5}{2}\varphi + q(\kappa)\varphi\right), \tag{8}$$

$$q(\kappa) = \frac{3}{4}\kappa\left(\int_{-1}^{1}\frac{x}{1+\kappa x}\mathrm{d}x + 1.5\int_{-1}^{1}\frac{1-x^2}{(1+\kappa x)(1+2\kappa x)}\mathrm{d}x\right).$$

The parameter G_1 is the effective shear modulus of the composite with the magnetically hard spheres, q reflects the addition to G_1 due to the magnetic field effect. The results of calculation of this parameter are shown in the figure 1.

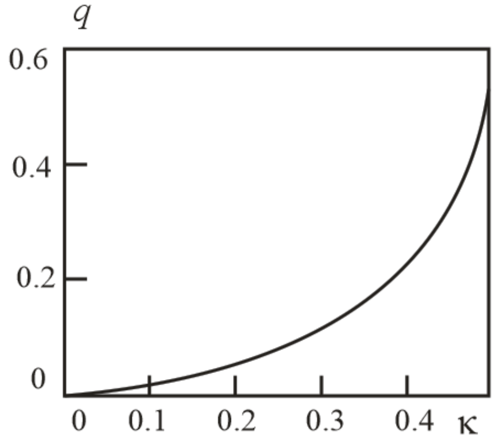

Figure 1. Parameter q in (8) versus the dimensionless magnetic field κ.

Within the framework of the used approximation, the effect of the magnetic field on the effective shear modulus of the composite can achieve about one fourth of the effect of the solid inclusions described by the Einstein term 2.5 φ. It should be noted that the situation when $\kappa \sim 1$ or more is beyond the approximation of small deformation inside the elastic matrix. The linear Lame equations cannot be used for the description of the particle rotation under the magnetic and mechanic torques for the large values of κ. The analysis of this case requires numerical solution of non-linear equations of the polymer matrix deformation.

3. Magnetically soft ellipsoidal particles

In this part we consider a system of ellipsoidal magnetically soft particles randomly distributed in an elastic matrix. For the maximal simplification of calculations and to get transparent physical results, we will restrict ourselves by the approximation of linearly magnetizable particles. The generalization to the nonlinear magnetization is not difficult, but leads to cumbersome calculations and final results.

We again suppose that the composite experiences the deformation of simple shear with the mean displacement $\boldsymbol{u}$ in the direction Ox and the gradient of the displacement along the axis Oz. The magnetic field $\boldsymbol{H}$ is aligned along the axis Oz.

By using the results of [26-28], we can present the component of the macroscopic shear stress as follows:

$$\sigma = G_0 \Big\{ 1 + \varphi \Big[\alpha + \tfrac{1}{2}[(\xi + \beta\lambda)(< e_x^2 > + < e_z^2 >) + \beta(< e_z^2 > - < e_x^2 >) + \\ +2(\chi - 2\lambda\beta) - < e_x^2 e_z^2 >]\gamma + \varphi g h^2 < e_x e_z > \Big] \Big\}, \tag{9}$$

$$\sigma = \sigma_{xz}, \quad \gamma = \frac{\partial u_x}{\partial z}, \quad g(r) = \frac{(\mu_\mathrm{p}-1)^2 (N_\perp - N_\parallel)}{(1+(\mu_\mathrm{p}-1)N_\perp)(1+(\mu_\mathrm{p}-1)N_\parallel)}, \quad h = \sqrt{\frac{\mu_0 H^2}{2G_0}}.$$

Here $\boldsymbol{e}$ is the unit vector aligned along the particle axis of symmetry; $\alpha, \beta, \lambda, \xi$ and χ are the functions on the aspect ratio r of the ellipsoidal particle (the ratio of the particle axis of symmetry to its diameter), μ_p is the particle relative magnetic permeability, $N_\parallel$ and $N_\perp$ are the demagnetizing factors of the particle along and perpendicular to its axis of symmetry respectively. The explicit forms of the shape-functions $\alpha, \beta, \lambda, \xi, \chi$ as well as of the factors $N_\parallel$ and $N_\perp$ are given in the appendix.

We present again the components of the vector $\boldsymbol{e}$ of an arbitrary particle as $e_i = e_{i0} + \delta e_i,\ i = x, z$. Because of the initial random orientation of the particles we get $< e_{i0}^2 > = \frac{1}{3}$; $< e_{x0} e_{z0} > = 0$; $< e_{z0}^2 > = \frac{1}{15}$. By using these relations in (9), in the linear approximation with respect to γ one can obtain:

$$\sigma = G_0\left\{1+\varphi[\alpha+\tfrac{1}{3}(\xi+\beta\lambda)+\tfrac{1}{15}(\chi-2\lambda\beta)]\gamma+\varphi g h^2(< e_{x0}\delta e_z > + < e_{z0}\delta e_x >)\right\}. \quad (10)$$

Following [27], one can present the equations for the vector $\boldsymbol{e}$ of an arbitrary particle as:

$$\delta e_x = \frac{1}{2}\gamma[\lambda(1-2e_x^2)+1]e_z - \psi e_x e_z^2 \quad (11)$$

$$\delta e_z = \tfrac{1}{2}\gamma[\lambda(1-2e_z^2)-1]e_x + \psi(e_z - e_z^3)$$

$$\psi(r) = h^2\,\frac{g(r)}{3\delta(r)} \#(12)$$

Here $\delta(r)$ is a function of the particle aspect ratio r. Its explicit form is given in the appendix. The parameter h presents the ratio of the magnetic and elastic torques acting on the particles. Similar to the previous case of the magnetically hard particles, the linear Lame equations of the small deformations of the elastic matrix are applicable only when the inequality $h < 1$ holds true.

Substituting the form $e_i = e_{i0} + \delta e_i$ into equation (11), after simple transformations, in the linear approximation we come to the relations:

$$< e_{z0}\delta e_x > = \frac{1}{2}\gamma\left[< \frac{Ae_{z0}}{1-\psi e_{z0}^3} > - \psi < \frac{2Be_{x0}e_{z0}}{(1-\psi e_{z0}^3)\big(1-\psi(1-3e_{z0}^2)\big)} >\right], \quad (13)$$

$$< e_{x0}\delta e_z > = \tfrac{1}{2}\gamma < \frac{e_{x0}B}{1-\psi(1-3e_{z0}^2)} > .$$

Here

$$A = [\lambda(1-2e_{x0}^2)+1]e_{z0}, \quad B = [\lambda(1-2e_{z0}^2)-1]e_{x0}.$$

Combining (10) and (13), we get:

$$\sigma = G_2\gamma G_2 = G_0\{1+\varphi f(r,h)\}, \quad (14)$$

$$f(r,h) = [f_1(r) + f_2(r,h)],$$

$$f_1 = \alpha + \tfrac{1}{3}(\xi+\beta\lambda) + \tfrac{1}{15}(\chi - 2\lambda\beta),$$

$$f_2 = \tfrac{3}{2}\psi\delta(r)\left[< \frac{Ae_{z0}}{1-\psi e_{z0}^3} > - h^2 < \frac{2Be_{x0}e_{z0}}{(1-\psi e_{z0}^3)\big(1-\psi(1-3e_{z0}^2)\big)} + < \frac{e_{x0}B}{1-\psi(1-3e_{z0}^2)} >\right].$$

Here G_2 is the effective shear modulus for the composite with the magnetically soft ellipsoidal particles. The term f_1 describes the effect of the rigid randomly oriented particles on this modulus; the term f_2 reflects the influence of the magnetic field H on G_2, the term f indicates the total effect of the particles on the elastic modulus G_2. For the spherical particles ($r = 1$) the relations, given in the Appendix, read: $\alpha = \frac{5}{2}$; $\beta, \lambda, \xi, \chi, \psi$ =0. Therefore, the Einstein formula $G_2 = G_0\left(1+\frac{5}{2}\varphi\right)$ for these particles is fulfilled.

Some results of calculations of the terms f, f_1 and f_2 versus the dimensionless magnetic field h as well as versus the particle aspect ratio r, are shown in the figures 2 and 3 respectively.

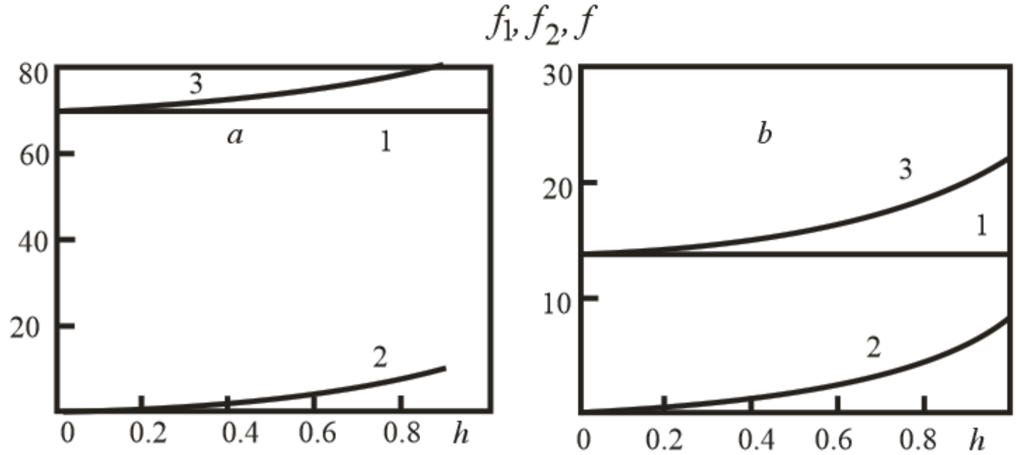

Figure 2. Parameters which determine the effective shear modulus G_s of the composite with the magnetically soft spheres vs. the dimensionless magnetic field h. (a) and (b) - the particle aspect ratio r = 0.01 and 10 respectively. Figures near the curves: 1 - f_1; 2 - f_2; 3 - $f = f_1 + f_2$.

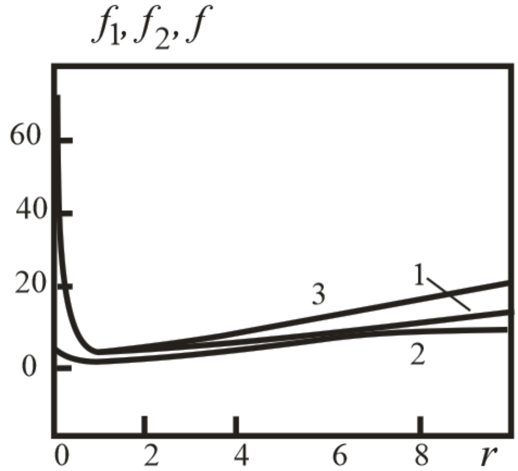

Figure 3. Parameters f_1, f_2, f vs the particle aspect ratio r. The dimensionless magnetic field $h = 1$.

These results demonstrate that the "magnetic" term f_2 can give the contribution to G_s very close to the "rigid particles" term f_1. This contribution is especially significant for the highly elongated particles ($r \gg 1$). For the oblate particles ($r < 1$) and the relatively weak fields ($h < 1$) the term f_2 is much less than f_1.

4. Conclusion

We present the results of theoretical study of effect of uniform magnetic field on the shear modulus of a ferrogels, consisting of magnetic particles randomly distributed in a polymer matrix. In order to achieve mathematically strict results, we have restricted ourselves by the analysis of the dilute systems and neglected any interactions between the particles. The results show that magnetic field increases the modulus and this effect can be quite comparable with the effect, provided by the particles as rigid inclusions in the composite. We believe that the results, obtained in the limiting case of the low concentrated systems, can be a robust background for the development of a theory of the moderately and highly concentrated soft magnetic composites. It should be noted that the we restricted ourselves by the spherical shape of the magnetically hard particles just for maximal simplification of mathematical part of the work. Combining the approaches, considered in the parts 2 and 3, one can easily generalize this analysis for the magnetically hard ellipsoids.

5. Appendix

The shape-coefficients $\alpha, \ldots \chi$ as functions of the particle aspect ratio r have the following form [25]:

$$\alpha(r) = \frac{1}{r\alpha_0'};\quad \beta(r) = \frac{2(r^2-1)}{r(r^2\alpha_0+\beta_0)};\quad \xi(r) = \frac{4}{r(r^2+1)\beta_0'} - \frac{2}{r\alpha_0'};$$

$$\chi(r) = \frac{2\alpha_0''}{r\alpha_0'\beta_0''} - \frac{8}{r(r^2+1)\beta_0''} + \frac{2}{r\alpha_0'};\qquad \lambda(r) = \frac{r^2-1}{r^2+1};\qquad \delta(r) = \frac{\beta(r)}{3\lambda(r)}.$$

Here

$$\alpha_0 = -\frac{1}{r^2-1}\left[\frac{2}{r} + \frac{1}{\sqrt{r^2-1}}\ln\left(2r^2-1-2r\sqrt{r^2-1}\right)\right];$$

$$\beta_0 = \frac{1}{r^2-1}\left[r - \frac{1}{2\sqrt{r^2-1}}\ln\left(2r^2-1+2r\sqrt{r^2-1}\right)\right];$$

$$\alpha_0' = \frac{1}{4(r^2-1)^2}\left[r(2r^2-5) - \frac{3}{2\sqrt{r^2-1}}\ln\left(2r^2-1-2r\sqrt{r^2-1}\right)\right];$$

$$\beta_0' = \frac{1}{(r^2-1)^2}\left[\frac{r^2+2}{r} - \frac{3}{2\sqrt{r^2-1}}\ln\left(2r^2-1+2r\sqrt{r^2-1}\right)\right];$$

$$\alpha_0'' = \frac{1}{4(r^2-1)^2}\left[r(2r^2+1) - \frac{4r^2-1}{2\sqrt{r^2-1}}\ln\left(2r^2-1+2r\sqrt{r^2-1}\right)\right];$$

$$\beta_0'' = -\frac{1}{(r^2-1)^2}\left[3r + \frac{2r^2+1}{2\sqrt{r^2-1}}\ln\left(2r^2-1-2r\sqrt{r^2-1}\right)\right];$$

The demagnetizing shape-factors $N_{\parallel}$ and $N_{\perp}$ are [28]:

$$N_{\parallel} = \begin{cases} \dfrac{r}{2(r^2-1)^{3/2}}\left[\ln\dfrac{r+\sqrt{r^2-1}}{r-\sqrt{r^2-1}} - 2\dfrac{\sqrt{r^2-1}}{r}\right], & r>1 \\ r\dfrac{r+\sqrt{1-r^2}}{2(1-r^2)^{3/2}}\left[\dfrac{\sqrt{1-r^2}}{r} - a\tan\dfrac{\sqrt{1-r^2}}{r}\right], & r<1 \end{cases}$$

$$N_{\perp} = \frac{1-N_{\parallel}}{2}.$$

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